Workshop Report on

Alternative Media, Conditions and Raw Materials

DRAFT

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Foreword

A little over a year ago Joseph Breen from the Green Chemistry Institute (GCI), and Nancy Jackson and Robin Rogers, Chair and Chair-elect from the Industrial and Engineering Chemistry Division of The American Chemical Society (ACS) – came forward expressing an interest in sponsoring a set of industry-led workshops. The workshops, in line with Technology Vision 2020, would focus on the need for new alternative, or "green" synthetic pathways for the chemical industry. This expression of interest corresponded to several meetings we had just completed in which we explored ways that our offices might undertake some activities of mutual interest. The timing of the request from ACS and GCI couldn't have been better. It seemed only natural that with energy efficiency and pollution prevention improvements for the chemical industry so closely related, we would join together to support ACS' and GCI's interest in a series of workshop sessions. And now we are pleased to learn that the results of the sessions will be used by ACS' Corporation Associates as the basis for a Vision 2020 roadmap on chemical sciences covering alternative synthetic pathways.

It is our hope that the far reaching and creative ideas contained in this preliminary report will continue to inspire the chemical industry as it strives to work for common goals that save energy, make the most efficient use of this country's carbon-based resources, protect the environment, and ensure the vitality of the industry well into the 21st century.

Signed

Denise Swink
Deputy Assistant Secretary
for Industrial Technologies,
Energy Efficiency and Renewable Energy
U.S. Department of Energy

Signed

Joseph Carra
Deputy Director
Office of Pollution Prevention and Toxics
Environmental Protection Agency

Dear Colleagues:

Technology Vision 2020 was published by the American Chemical Society (ACS) in 1996. The report, developed by several hundred U.S. technical and business leaders, and representatives from The Chemical Manufacturers Association (CMA), the Synthetic Organic Chemical Manufacturing Association (SOCMA), the Council for Chemical Research (CCR), the American Institute of Chemical Engineers (AIChE), and the ACS, describes a future where the chemical industry will lead the world in technology development, manufacturing and profitability. It will also be an industry that seeks opportunities to improve energy use and environmental stewardship by conducting breakthrough R&D. The **Vision** says the next millennium will see a chemical industry that promotes sustainable development by investing in technology that protects the environment and stimulates industrial growth while balancing economic needs and financial constraints. And the **Vision** calls for an industry that will set the standard for efficient use of energy and raw materials and work in seamless partnerships creating "virtual" laboratories for developing innovative technologies.

To this end our mutual organizations sponsored four industry-led workshops during 1998, as our contribution toward the goals of **Vision 2020**. The workshops brought the industrial, academic, and government research communities together to generate new ideas for developing alternative, environmentally benign, or "green" technologies. These gatherings allowed researchers from universities and government laboratories to speak directly with industrial process users and help solve their production problems as well as identify new opportunities for alternatives. Clearly, a collaboration among industry, academia, and government represents an important approach to leveraging available resources...those same resources that will be required to achieve an economic and environmentally-efficient chemical industry for the 21st century.

We *sincerely believe* that the subjects covered in these workshops, chemical synthesis and processing with alternative reaction media, conditions, and raw materials is central to the successful implementation and achievement of the **Vision 2020** goals. We *sincerely believe* that some of these new approaches to chemical processing represent a better way to protect our environment, save energy and make the most efficient use of our carbon-based resources. We *sincerely believe* that these ideas for new technologies will enable a greater improvement in human and environmental health than the technologies currently in place. And finally we *believe* that these efficiencies will result in reductions in toxic dispersions and the energy and material intensity of goods and services; improvements in product durability and material recyclability; and an increase in both the sustainable use of renewable resources and the service intensity of goods and services.[1]

This report represents results of all four workshops. We thank the Energy Department's Office of Industrial Technologies (OIT) and Environmental Protection Agency's Office of Pollution Prevention and Toxics (OPPT) for their support. We hope these workshops will make a contribution toward achieving the industry's **Vision,** layout some of the ground work needed to build a comprehensive national research agenda, and, in turn, help change the way people think about the chemical industry. The chemical community's work toward a roadmap, however, does not end here and we urge you to keep informed and become involved in this ongoing process. Further information about **Vision 2020** activities, including the Technology Roadmaps and outcomes when available, can be found on the ACS I&EC webpage at http://membership.acs.org/i/iec/; the Green Chemistry Institute webpage at http://www.lanl.gov/Internal/projects/green/; the AIChE Vision 2020 webpage at http://www.aiche.org/cwrt/projects/, and the CCR site at http://www.ccrhq.org/v2020/.

Joseph J. Breen
Executive Director
The Green Chemistry Institute

Robin D. Rogers

[1] Eco-efficiency: The Business Link to Sustainable Development, Livio D. Simone & Frank Popoff, World Business Council for Sustainable Development, MIT Press, p.56, 1977.

Chair, American Chemical Society
Industrial & Engineering Chemistry Division

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- National Environmental Technology for Waste Prevention Institute
- Center for Industry Research on Polymers

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Contributors

Industry

A.E. Staley Manufacturing
ARCO Chemical
AGA Gas
Air Products & Chemicals
Akzo-Nobel
Autoclave Engineers
BCI
BF Goodrich
Biofine
BOC Gases
Chemical Information Services
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Universities

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1 Introduction

Meeting the Chemical Industry's Goals for the 21st Century

In 1996, over 200 technical and business leaders from the U.S. chemical industry culminated a series of working meetings with the publication of **Technology Vision 2020: The U.S. Chemical Industry**[2]. The report addresses many factors affecting the chemical industry's competitiveness and the allocation of federal R&D funds devoted to advancing the manufacturing base of the U.S. economy. The **Vision** identifies globalized markets, environmental performance, profitability and productivity, customer expectations, and changing workforce requirements as the "five major forces" confronting the industry as it enters the 21st century. Further, the report describes a chemical industry in the 21st century that will lead the world in technology development, manufacturing, and profitability as well as be responsible for breakthroughs in R&D that improve energy use and environmental stewardship.

The **Vision** calls for the industry to set the standard for the efficient use of energy and raw materials and work in seamless partnerships, creating "virtual" laboratories for developing innovative technologies. The study says that the next millennium will see a chemical industry that promotes sustainable development by investing in technology that protects the environment and stimulates industrial growth while balancing economic needs and financial constraints. <u>Technology Vision 2020: The U.S. Chemical Industry</u> concludes that the synergy of collaboration often has a "multiplier effect" on our nation's pool of talent, equipment, and capital available for R&D and that the chemical industry's growth and competitive advantage *"depends upon individual and collaborative efforts of industry, government, and academe to improve the nation's R&D enterprise."*

Clearly these far-reaching goals for improved productivity, cost-effectiveness, energy use, and environmental performance will require that the industry address both improved, as well as radically new or alternative ways of making chemical products. Finding the best alternative process will call for the discovery and integration of more than one new technology or the improvement in more than one manufacturing process.

Defining a Role For Alternatives

Every industrial process used to manufacture a chemical product begins with a set of chemical reactions where each reaction is characterized, in part, by the **raw materials** or feedstocks; the **reaction media,** or the substance that allows the raw material molecules to dissolve; and the **reaction conditions** or what

2 Available from the American Chemical Society, Washington, D.C., (202) 452-8917.

makes the reaction "go." Groups of reactions toward a product are sometimes referred to as a pathway. An *alternative* synthetic pathway should be more environmentally benign than the pathway currently in use. But the benefits of applying an *alternative* should go beyond improving the environment. An alternative process in industry should also achieve more efficient use of precious resources (e.g., energy, raw materials), reduce the production of unneeded by-products and waste, and improve manufacturing productivity. (See Exhibit 1)

Exhibit 1. Selected Examples of Alternative Media, Conditions and Raw Materials

Media	*Conditions*	*Raw Materials*
dense phase supercritical ionic aqueous solventless	microwave electrochemical radio frequency ultrasonic plasma radiation induction photochemical catalysis interfacial/surface mediated	C_1 molecules *from* biomass; biomimetic- synthetically derived waste and residues; and atmospheric emissions

Using these criteria researchers in industrial process improvements will follow a number of "paths" on several levels simultaneously. On the first level successful alternatives for source reduction and energy saving results will be obtained by taking a systems approach that combines and as many desirable pathways as possible. On the second level, the inextricable connection between media, conditions, and raw materials will mean that a change in any one of the reaction's components will most likely require some number of supporting or compensatory changes elsewhere in the immediate reaction..

Designing a new synthetic pathway to manufacture chemical products means the researcher must, among a number of other variables, identify and select the best mix of media, conditions, and raw materials. Clearly the challenge of creating energy efficiency, environmental benefits and enhancing the economic viability of the U.S. chemical industry around the world begins with early, up front planning at the molecular level.

Meeting the Challenge

In keeping with **Vision 2020**, the Industrial and Engineering Chemistry Division of ACS and the Green Chemistry Institute sponsored a series of workshops to explore the potential for using alternative synthesis in the chemical process industries. Additional support was provided by the U.S. Department of Energy, the U.S. Environmental Protection Agency, and the Electric Power Research Institute. The workshops were attended by participants from industry, government, academia, and the national laboratory complex (a complete list of individual participants is provided in appendix A). Each workshop focused on a separate reaction area:

- Alternative Media Workshop, Sante Fe, New Mexico, April 13-16, 1998: alternative reaction media, alternative cleaning and dissolution, and materials modification/pollutant sequestration.

- The Role of Polymer Research in Green Chemistry and Engineering, Amherst, Massachusetts, at the University of Massachusetts, June 11-12, 1998: modeling and simulation of new polymers, synthesis and catalysis of environmentally benign polymers, benign processing for polymers.
- Electro technology and Alternative Process Conditions, Houston, Texas, October 19-20, 1998: use of electro technologies and alternative conditions for chemical processing.
- Synthesis and Processing with Alternative Resources, Denver, Colorado, December 9-11, 1998: science, processing and engineering for chemicals from alternative raw materials.

In each workshop participants discussed industry opportunities, performance targets for the future, key technology barriers and priority research needs. Participants were asked to look ahead as far as 2020, and to generate "out-of-the-box" ideas that could potentially be achieved within this time frame. We have done our best to accurately capture the observations and ideas from these discussions on the following pages.

2 Barriers to Development of Alternative Technology

Exhibit 2-1. Key Barriers to Development and Use of Alternative Cleaning and Dissolution Methods
(◆ = Most Critical Barriers)

Process & Equipment Engineering	Chemical Science & Theory	Institutional Issues	Market/Economic Issues
Lack of suppliers and manufacturing capacity for this equipment ◆◆◆◆ – high cost of high pressure equipment Lack of understanding of CO_2 properties for design of process products – high pressure – low temperature – interaction with CO_2 as media Lack of service/ organizations technicians trained to service and maintain equipment (high pressure)	Lack of material compatibility data with CO_2 and other DPF ◆◆◆◆◆◆ – lack of equipment capable of handling DPF at low temperatures Lack of understanding of DPF chemistry and processes ◆◆◆◆ – colloids – operating at lower pressures – co-solvents – other additives Large cost and time of experimental programs/lack of computer process simulation models ◆◆ Infinite number of poorly defined or proprietary contaminants that must be addressed Lack of engineering standards and guidelines on best practices	Users/customers are widely distributed and technically inexperienced ◆ Improper application of technology by end users Overcoming inertia association with existing technology Lack of funding to identify new applications of alternate cleaning methods – difficulty in finding seed funding for smaller, niche applications (e.g., contact lens cleaner) Lack of standards and care symbols – garment cleaning	Lengthy time to market may result in introduction of less green, or non-green technologies Focus on large users (only 10% of market) may shut out smaller users – tendency to focus on large users Lack of case studies and commercial successes Early demonstration failures that inhibit development Lack of efficient lo-cost distribution networks for dense phase fluids by application – distribution cost is currently fairly high Lack of understanding of green economics (life cycle analysis, etc.)

Exhibit 2-2. Barriers to using Alternative Reaction Media in Chemical Synthesis

(◆ = Most Critical Barriers)

Innovative Chemistry

Lack of examples of better new chemistries
◆◆◆◆◆
- new material properties
- new routes to old chemical products
- new chemical products (non-incremental)

Lack of ability to design surfactants/ address solubility problems
◆◆

Insufficient ability to perform product isolation from ARM ◆◆

Too many synthetic steps to produce and isolate products
◆

Lack of co-solvents to use with CO_2
◆

Low space/time yield

Poor suspension of solids in low-viscosity fluids

High cost of biomimetic chemistry

Poor understanding of activity of products as they impact recovery in ionic fluids

Inability to control morphology of advanced materials

Process/ Equipment Engineering

Lack of creative engineering
◆◆◆

Lack of optimization tools
◆◆

No means to introduce and remove solids (batch to continuous)
◆

No way to reduce the change in pressure barrier for dense phase fluids
◆

Unresolved material compatibility issues
◆

Lack of under-standing of ARM technology fit
◆

Lack of understanding of the scale-up route for equipment

No standards for reactor design for dense phase fluids

Uncertainty over corrosion behavior in materials of construction of process equipment

Reactors that are too expensive and not optimized

Lack of off-the-shelf equipment and routine repair infrastructure

Limited suppliers of equipment/ lack of demand

Inadequate energy management

Un-optimized process design

Lack of scale-up concepts in reactor engineering for dense phase fluids

Media handling problems

- chemistry, materials, solids formation, corrosion, economics

Chemical Science & Theory

Lack of data/predictive models
- solubilities, viscosities, density, heat capacity, phase diagrams, toxicology

◆◆◆◆◆◆

Lack of knowledge of thermophysical properties (i.e., data on phase behavior)
◆◆◆◆

Lack of funds for chemical research
◆◆◆◆

Lack of knowledge of reactivity and kinetics in dense phase fluids/ARM
◆◆

Limited chemical engineering data
◆◆

Insufficient understanding of function of catalysts
◆◆

Limited understanding of mixing/diffusion/ flow dynamics for ARM processes
◆◆

Lack of knowledge on how medium affects catalyst
◆

Lack of knowledge of the nature of solvation for ionic anc non-ionic liquids
◆

Insufficient accessible database of information related to ARM
◆

Lack of data on feedstocks
◆

Lack of screening tools for ionic liquids

Lack of mixing and transport knowledge (heat and mass)

Poor understanding of physical and chemical behavior of dense phase fluids/ARM

Institutional Issues

Focus on CO_2 may diminish interest in other fluids
◆

Lack of effective communication: between international industry and among industry/academia, and labs
◆

Lack of testing facilities and equipment in industry for dense phase fluids/ARM

Lack of detailed strategy for implementation

Lack of concurrent, multi-disciplinary work

Insufficient education supporting application and research of alternative media, phase transfer catalysts, etc.

Poor interface between chemical industry and process design in equipment industry

Lack of skilled researchers

Stringent regulatory climate

Market/ Economic Issues

High capital cost of alternatives
◆◆

Lack of overall system economic assessment (no simple tools available for researchers)
◆◆

Poor under-standing of ultimate effect of process change on product
◆

Limited reporting of successes and industrial demonstrations
◆

Competition vs intellectual property issues
◆

Inability to manage risk
◆

Inability to measure benefits effectively
◆

High maintenance costs

Inability to conduct life cycle analysis on new ARM processes

Lack of an accepted benchmark

High uncertainty regarding costs of implementing dense phase fluids/ARM

Benefits not proven to exceed technical risk

Lack of information on advantages of ARM (models are inadequate, right tools are not available)

Long implementation time

Exhibit 2-2. Barriers to using Alternative Reaction Media in Chemical Synthesis (◆ = Most Critical Barriers)				
Innovative Chemistry	**Process/ Equipment Engineering**	**Chemical Science & Theory**	**Institutional Issues**	**Market/ Economic Issues**
	Lack of controls/sensors for new reactors	Lack of knowledge of corrosion in dense phase fluids/ARM Lack of data needed for economic evaluation and scale-up Incomplete understanding of supersaturation - (physical chemistry behavior)		Unknown economies of scale No common metrics

Exhibit 2-3. Barriers to Material Modification & Pollutant Sequestration Using Alternative Media (◆ = Most Critical Barriers)			
Process & Equipment Engineering	**Chemical Science & Theory**	**Institutional Issues**	**Market/Economic Issues**
Lack of standardization and standardized equipment components ◆◆◆ Inadequate methods for choosing best the additives ◆ – poor understanding of thermodynamics Systems for automated feeding of solids into high pressure vessels do not exist ◆	Inability to predict thermo-physical properties ◆◆ – phase behavior – thermodynamics – mechanics – kinetics – hydrodynamics – solution (local) structure – local (micro) thermodynamics – mass transfer Lack of non-equilibrium data ◆◆	Lack of model for industrial/government/academic collaboration ◆◆◆ Amount and stringency of regulations ◆◆ Lack of education ◆◆ – financial institutions (investors) – consumers – students – policy/law makers Lack of global view ◆ Political barriers Lack of baseline to define pre-competitive research ◆	Limited waste and cost information ◆◆ Development risk and expense conflicts with technology transfer ◆ – cost of performance is not paid by beneficiary No methods available for placing value on waste Uncertainties in product stewardship Lack of materials -- in sufficient quantity or cost Some waste is currently cheaper to dump than recycle Inadequacy in the way social costs are assessed Cost uncertainties – operating costs – environmental cost/benefit – equipment costs Lack of incentives – tax structure Applications developers lack understanding of key supplier industries

Exhibit 2-4. Technical Barriers to the Use of Electrotechnologies/ Alternative Conditions in the CPI

(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Process Engineering	Chemical Science
Scale issues ✪✪✪✪✪●●●●●○ – too much entrenchment in large processes – difficulties scaling up solvent-less processes – difficulty in scale up due to short penetration depths for microwave and ultrasound Lack of efficient separations for – dilute solutions (hydroquinous bioprocesses) – electro-synthesis ✪✪✪●●○○ Difficulties in adapting biological processes ●● – scale issues – amount of product – has not been applied to bulk chemicals – most end-users are not chemical engineers Inability to adapt equipment design for alternative technology (e.g., microwave reactors)● Lack of durable, robust technologies (i.e., demonstrated to last years with minimal maintenance) ● Difficulty in adapting electrosynthesis to many important applications, especially those with liquid/solid interfaces High cost of on-demand sensors/controls (development costs)	Lack of understanding of electrochemical surface phenomenon ✪✪✪●○ – interfacial conditions – transfer catalysis – at solid liquid or liquid/liquid interface rather than bulk Poor understanding of reactions between electricity, magnetic fields, and membranes ✪✪✪ Poor understanding of heterogeneous reactions ✪●● Lack of support for developing data for process applications (e.g., physical properties and reaction mechanisms) ✪✪○○○○ Microwave effects are not fully understood ✪●○○ Lack of data in non-aqueous electrochemistry ✪● Lack of understanding on how to control reactions at the surface of electrodes ●●○ Insufficient knowledge of how to apply photochemistry to industrial chemicals ○○ Lack of multi-unit microbiological process trains to sequence reactions with a series of microorganisms ✪ Insufficient atomic force field database for molecular modeling ● Lack of understanding of computational mechanistic chemistry for stereochemical reactions ●○○ Insufficient chemical data to support new technology development ● Inability to effectively balance modeling and experimentation efforts ○○○○ Lack of data for life cycle models ○ Inadequate knowledge of dipolar mixtures ○○ Insufficient data for analyzing electrosynthesis and comparing with conventional methods (e.g., electrode potentials, energy impacts) Poorly understanding of electrochemical processes (e.g., reaction mechanisms) and inability to control process Inadequate fast computation algorithms for molecular modeling to achieve faster, accurate calculations

Exhibit 2-5. Technical Barriers to the Use of Electro technology/ Alternative Conditions in the CPI
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Specific Technology Issues	Energy and Power Sources	Materials	Catalysis
Meager engineering understanding of electrochemical cell design ✪✪	Lack of socially acceptable nuclear power generation ✪✪✪●○○	Electrotechnologies are materials-limited ✪✪ – membranes foul easily – electrical materials are not stable	Catalysis is not well understood ●●○ – electro-catalysis is very poorly understood ✪✪●●●
Lack of H_2O_2 production technologies (in situ or storage) ●○○	Lack of energy storage technology ✪✪✪●	Insufficient membrane technology (e.g., solid electrolyte membranes) ●●○○	Lack of efficient catalysts for moving electrochemicals to photochemical processes (change to the visible range) ✪✪●○○
Inability to easily make packed bed electrodes ●○	Lack of efficient hydrogen storage medium (compression of H_2 is expensive and dangerous) ✪○	Inability to fabricate ductile non-brittle, glass-like material with photochemical process capability ●●	Lack of innovative electrocatalytic nano-reaction site design ○
Unavailability of micro-electrolytic cells ●	Lack of efficient energy delivery systems ✪	Lack of predictability in ceramics design and processing (e.g., insulators, vessels) -- no good net shape process to reduce failure flaws ○	Over-reliance on precious metals for catalysis ●
Lack of efficient advanced oxidation technology ●	Lack of economies of scale in electrical processor equipment ✪	Lack of construction materials (especially electrodes) for production scale-up	Lack of inherently active catalysts
Lack of adequate solvent systems/supporting electrolytes ○	Lack of appropriate materials for fuel cells (membranes, catalysts) ○○		Lack of biomimetic catalysts that utilize H_2O_2 and/or O_2
Electro-synthesis (with liquid diffusion coefficients) cannot compete with conventional gas diffusion on a cost basis ○	Lack of modular, efficient, low-cost residential and commercial solar energy sources ○		
Lack of tuneable laser systems for chemistry investigations and system design	Inability to transport energy as a “field” ○		
Lack of efficient long-life photochemical lamps (more UV, less IR)	Lack of “on-board” generation of hydrogen from water vapor		
Lack of appreciation for plasma use in large scale operations due to cross-disciplinary communications barriers	Electrochemical processes will require more efficient power systems ○○		
	Lack of purification process to avoid poisoning of fuel cells (hydrogen-specific membranes)		
	Lack of inexpensive remote power sources for self sufficiency		
	Lack of breakthrough power source such as real cold fusion		
	Lack of safe, high yield fuel cell technology		
	Lack of highly efficient distributed resources with excellent stability and power quality for site-specific independent power		
	No H_2 delivery infrastructure for fuel cells		
	Perception of hazards associated with H_2 fuel cells		
	Lack of solid fuels (e.g., gels)		
	High cost of new systems for hydrogen		

Exhibit 2-6. Non-Technical Barriers to the Use of Electrotechnologies/ Alternative Conditionsin the CPI

(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

General Investment/Decision-Making	Marketing and Policies
Lack of knowledge for determining if electro-technology is providing new/better chemistry ✪✪✪✪✪○●	Too much technology push versus customer pull ✪✪●
Chief executives are driven by money-managers (step change technologies are not popular investments) ✪✪✪●	Policy and markets do not drive new technology and technology substitutions
Lack of demonstrated successes ✪✪✪✪✪	Technology only advances through capital investment which is implemented only when industry is ready -- the focus has been on just adding capacity
Already existing capital investment ✪✪✪●	Lack of “industrial park” approach to total resource use/reuse/recycling for incremental process plant changes
Lack of “green screen” framework for evaluating and optimizing economic, energy, and environmental options. Framework is needed so science is not conducted in a vacuum (similar to the IPAC equation to evaluate societal economic needs) ✪✪○○	A regulation approach to encouraging “green” processes is unlikely to succeed
Management/industry aversion to risk ✪●●●●	Current paradigm of economic value lacks a long term vision
Economic, environmental benefits of alternatives, including electrotechnologies, are not available ✪✪✪✪✪✪○○	
Risk-reward is not clear/uncertain to management ✪●●	
Unsuccessful past attempts to apply electro-technologies to chemicals and refining ✪●●	
Lack of virtual “consultative” relational database (virtual model) for basic research information to support electrotechnologies in chemical processes (interactive training, expert advice, non-competitive scope, user friendly interface) ✪○●○	
High capital costs of new processes ●	
Lack of date for comparing efficiency versus “green” impacts for chemical, electrochemical, and biochemical processing ○	
Lack of maturity of new technology so decision makers are uncomfortable investing ○	
Lack of a neutral demonstration site to explore science, engineering, economic and infrastructure issues	
Lack of understanding of the economies of rebuilding plants with new technology	
Lack of clearinghouse for information on research, potential problems, industry experience with new technology	
Lack of decision-making tools to estimate electrochemical efficiency onsite (e.g., life cycle analysis)	

Exhibit 2-7. Non-Technical Barriers to the Use of Electrotechnologies/ Alternative Conditions in the CPI (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)	
Education and Institutional Issues	**R&D Funding**
Lack of basic training/ education in electrochemistry ●●●●●● Inadequate communication with electrochemical equipment suppliers ✪●● Inability to get different disciplines (chemical engineers, researchers, chemists, biologists, electrical engineers) to communicate and work together ●●○○○ Regulatory environment that makes some development difficult ○○ Control of intellectual property ○ Lack of cooperation between industry/government, industry/industry Culture shock in moving from conventional processes to electro-process Lack of visionaries in the corporate community to advocate new technology	Lack of focus on fundamental thinking - changes in the nature of industrial R&D ✪● Insufficient/inconsistent funding for energy research ● Roller coaster funding for science is focused on addressing long-term problems ○ Decreasing availability of R&D funds Diversity of chemical industry and disparity in funding for R&D Lack of research teams supported to focus on identified problems

Exhibit 2-8. Barriers To Polymer Modeling (◆ = Most Critical Problem Areas/Barriers)				
Computing Ability	**Human Institutional Factors**	**Basic Knowledge/ Science**	**Lack of Data**	**Clearer Definition**
Getting around molecular size problem - size/accuracy trade off ◆◆◆ – scan length and time scales (micro to macro)	Attitude towards use and trust of simulations ◆	Lack of basic science - understanding of ◆◆	Lack of good physical property data ◆◆◆ – kinetic data	Fuzziness of product description
Computer Hardware – speed ◆	Common understanding of what modeling is ◆	Need models that take processing history into account ◆◆	Lack of micro-structure and defect information ◆	What is “green” in 2020
Lack of development of force fields to allow modeling of certain properties ◆	Ease of usability of models ◆ – in-house theoretical development – platform independent	Complexity and diversity of reactions ◆ – reactants – blends – product		
Ability to model wear ability and durability ◆	Cost	3-D crystallinity (length scale)		
Lack of hybrid modeling methods (w/communication between different methods)	Excellent minds are leaving polymer modeling chemistry (theoretical physics)	Lack of understanding of interactions with additives		
Optimization methods/techniques for “many degree of freedom” problems	Missing out on transferring accomplishments from other industries	Measuring chemical and physical characteristics of material in situ		
Lack of method to model recycle ability of materials	Lack of cross-discipline approach	Quantum modeling of transition metals		
	Timing of <u>modeling</u> common understanding	Need better understanding of fluid mechanics of mixing, shear fields, wall effects, etc. – reactor flow modeling with CFD		
	Understanding limitations and output of modeling	Need way to model toxicity		
	Interface between modeling and marketing departments	Problems in photo degradation (modeling of)		
		Need advances in process models for model-based control – mechanisms to respond to changes		
		Quantitative structure - property relations (structure-based)		

Exhibit 2-9. Barriers To Alternative Polymer Processing/Synthesis (◆ = Most Critical Problem Areas/Barriers)					
Institutional/ Educational	**Technology Issues/ Existing/Other New Polymerization**	**Technology-Other Issues/National Polymers**	**Basic Science/Predictive Capability**	**Customer Needs Market Demands**	**Other**
Lack of apparent national priority "all talk...no $" (e.g. funding for chemical knowledge ◆◆◆◆◆◆◆ Risk-Aversion in present chemical industry ◆◆◆ Public awareness issues ok "green" polymer issues ◆◆ Lack of integrated education biochemistry/polymer ◆ Lack of funding for modeling enzymatic/genetic approaches ◆ Social science/polymer science communication problems ◆ MBA mentality in industry Biochemistry/polymer chemistry inter disciplinarian approach needed Regulatory issues/product approval time Improved interaction between polymer synthesis and catalysis areas Public understanding of genetic engineering Ability for "Start Up" companies to develop technology – capital available government support	Cost of "green" manufacturing ◆◆◆◆◆◆◆◆◆ Cheap energy costs–petroleum based ◆◆◆◆ Reduce discovery to commercialization time ◆◆ Catalyst--supported catalyst activity problems ◆ Concept/reality not effective for many "green" ideas. Analytical capabilities to support new processes. Need to understand problems with new "green"synthesis	Lack of separation processes for bio-mass based processes ◆◆◆ Scale-up issues for genetically designed polymers ◆ Fermentation –need cell-free systems ◆ Lower cost delivered by bio-mass–not available now Arable land for bio-mass feed stocks Developing nations renewable resources specific to area–no infrastructure for biodegradable polymer wastes Bio-mass technology not developed to commercial feasibility Integrated process for complete feed-stock utilization Bio-mass technology–no infrastructure high initial cost Development of 100% reliable processes	Lack of knowledge of biosynthetic pathways ◆◆◆◆ Computational chemistry need improvements – improved models – computational speed ◆◆◆◆ Understanding of polymer self-assembly ◆◆ Polymer structure/bio-activity/bio-degrade ability relationships? ◆◆ Predictive/modeling of enzyme activity for chemical/ polymer reaction ◆ – lack of enzyme mimetics Lack of combinatorial strategies for polymer development ◆ Genetic pathway manipulation to produce polymers-understanding needed Definition of what the fundamental research needs actually are Adaptation of biomemitic concepts to new material synthesis	Definition of key requirements for specific applications Limited need for new materials Lack of customer Genetic pathway manipulation to produce polymers–understanding needed demands	Lack of new/creative ideas

Exhibit 2-10. Barriers to Benign Processing and Alternative Reaction Media for Polymers
(◆ = Most Critical Problem Areas/Barriers)

Physical/ Chemical Properties	Chemical science Knowledge	Marker/ Economic Issues	Engineering & Equipment	Institutional Issues	Education/ Training
Low mobility in low solvent systems ◆◆ – heat/mass transfer Lack of good compatibilization technologies for mixed polymer stream recovery ◆ Incompatible properties of polymer materials ◆ Tradeoffs between low solvent versus low energy Volatility of monomers without solvent Different compounds are not miscible Thermal instability of most polymers Negatives associated with molecular weight Limited solvent power of CO_2	Few candidates that are "green" reaction media ◆◆◆◆◆◆◆◆◆ – lack of supportive thin-liquid films Structures processing, property relationships are not fully understood ◆◆◆ Absence of chemical science data ◆ Lack of understanding of current, non green processes ◆ Don't have catalysts to allow CO_2 as feeds back Lack of lists/libraries – polymer processing aides – green A.R.M. Don't have continuous processes Don't know appropriate reaction conditions	Lack of incentives outside of regulatory areas for investing resources ◆◆◆◆ Lack of competitive advantage – lack of drivers ◆ LCA lacks numerical impacts High cost of research (mostly development) Cost of retrofitting equipment Lack of developed markets for green products Lack of infrastructures and markets for post consumer polymer recycling Capital cost is too high Lack of consumer acceptance for higher cost, green products	Lack of infrastructure for CO_2 use (and other super critical fluids) – room temperature ionic liquids – nano phase – supported liquid films Inability to fabricate cost-effective high pressure equipment Lack of instrumentation for online processing Lack of high vacuum equipment (cost-effective) Green chemistry/products tend to make processes more difficult Don't have continuous processes	Lack of definition of "green" or "environmental benign" ◆ Is holding CO_2 back to efforts to look at other benign materials Lack of management support for research and development – short term profit motive Lack of support for projects that do not meet regulatory needs Lack of a consistent definition of green chemistry Reluctance to change existing processes	Lack of personnel trained with using super critical CO_2 or other green technologies

Exhibit 2-11. Barriers/Alternative Raw Materials/New Science

(◆ = Most Critical Problem Areas/Barriers)

Properties	Policy & Strategy	Processes & Separation	Bio-Related	Catalysis	Computational	Synthesis	Photo-Chemical (biosynthesis)
Lack of understanding of structure and function relationships (monomers and polymers) ◆◆◆ Liquid diffusion coefficients are limiting ◆ Thermodynamic problems - - CO_2 is stable and difficult to activate ◆ Lack of detailed phase behavior studies for multi-component systems ◆ Lack of understanding of property relationships along pathways from raw material to final products High oxygen content of alternative material	Abundance and diversity of established petrochemical-based raw materials ◆◆ Lack of access to computational modeling for small companies ◆ No long-term government spending on chemical processes ◆ No structures in congress and universities to support longer-term R&D and underwrite R&D risks ◆ Difficulty educating decision makers about the value of chemical research (research is not all done) Lack of industry guidance for directing lab and university R&D – how can industry guide longer term research without compromising proprietary information	Lack of separation and handling technology for processing and extraction from large volumes of biomass and H_2O (field to end product in large volume) ◆◆◆◆◆◆ Absence of low-cost biomass pretreatment processes that: – yield fibers reactive to enzymatic hydrolysis – do not generate fermentation inhibitors – do not degrade carbohydrates and a lack of related fundamental understanding ◆◆◆◆ Lack of mechanisms to deploy polymers ◆◆ Cost of separation technology for multi products derived from alternative sources ◆ Lack of cost-effective co-generation of power/ chemicals at specific regional sites	Lack of ability to engineer an entire metabolic pathway ◆◆◆◆◆◆ Low space time yields for bio-process ◆◆◆◆◆◆ Lack of understanding of how to link protein sequence to structure; structure to sequence; structure to function and vice versa ◆◆ Little or undefined co-product opportunities ◆ Lack of designed or isolated enzymes that can function at high or low pH ◆ Inability to control growing plant structure ◆ Lack of ability to engineer biomass to make it easy to convert ◆	Lack of catalysts for activating small molecules especially CO_2, CO, O_2, N_2 ◆◆◆◆◆◆◆◆◆◆◆ Lack of selective oxygen catalysts using O_2 or H_2O_2 ◆◆◆◆◆◆◆◆ Time consuming lignin synthesis (homogenous catalysts) ◆◆◆◆◆◆ Lack of understanding of catalysts for the conversion of biomass ◆◆◆◆ Lack of understanding of catalysts involved in activating and coupling C_1 raw material ◆◆◆ Lack of C-H and C-C bond activation ◆◆ Lack of catalysts to enable processes with fewer persistent	Lack of understanding of mechanistic reactions and ability to model to eliminate trial/error in catalyst design ◆◆◆◆◆◆◆ Lack of computational tools for chemical and biological pathways Improved use of computational methodology for catalyst design, including designing predictive product stability	Cheap H_2O_2 (cheap as $C1_2$) ◆◆◆◆◆ Inability to differentiate sites on a carbohydrate ring for selectivity control ◆ Corrosive reagents and/or excessive pressure and C1 chemistry in C-C bonds	Lack of ability to gather and use solar radiation efficiently ◆◆◆◆◆◆◆ Lack of technology for photo-generation of H_2 ◆ Absence of better catalysts to capture solar energy

Exhibit 2-11. Barriers/Alternative Raw Materials/New Science (◆ = Most Critical Problem Areas/Barriers)							
Properties	**Policy & Strategy**	**Processes & Separation**	**Bio-Related**	**Catalysis**	**Computa-tional**	**Synthesis**	**Photo-Chemical (biosyn-thesis)**
	Lack of logistical infrastructure for handling and transporting alternative resources Lack of farmable land for dedicated biomass Lack of mutual understanding between chemists biologists on problems and needs Lack of logistical infrastructure for recycling polymers Industry is risk adverse and short-term focused Lack of balance in universities on combining fundamental thinking (enough to lead to new understanding) with innovation (up stream invention process)	Inability to couple a thermo-dynamically allowed reaction with a thermo-dynamically not allowed reaction (without making salts) Lack of syngas plants that can operate on a small scale	High cost of cellulase enzymes – absence of microbes that produce cellulase in conjunction with products of interest ◆ Lack of knowledge of microbe expression systems Lack of under-standing of stability and activity of biocatalysts Too many co-product schemes (vice versa) – have to sell all of them – tunability Lack of cost effective synthesis routes for the production of fuels, chemicals or fuel additives from biomass Lack of microbes that are selective, robust, productive, product tolerant and cheap	pollutants ◆◆ Lack of catalytic disinfection technology based on O_2 or H_2O_2 ◆ Inability to get around kinetics with catalytic design Lack of high thru put methods for catalyst design Lack of understanding of surface science for building blocks derived from alternative raw materials Lack of ability to deliver energy to catalyst site while preserving selectivity Lack of electro-catalysts that can harvest the majority of energy in chemicals as usable electrical energy Absence of electro catalysts for processing complex fuel (store energy as chemical			

Exhibit 2-11. Barriers/Alternative Raw Materials/New Science (◆ = Most Critical Problem Areas/Barriers)							
Properties	**Policy & Strategy**	**Processes & Separation**	**Bio-Related**	**Catalysis**	**Computa-tional**	**Synthesis**	**Photo-Chemical (biosyn-thesis)**
				e.g. methanol) Lack of catalysis for H_2 generation and recovery Difficulty in achieving M-C bond formation from CO_2 and M (metal)			

Exhibit 2-12 Barriers/Alternative Raw Materials/Processing Alternatives
(◆ = Most Critical Problem Areas/Barriers)

Cost Issues	Social Political Barriers	Feedstocks	Products	Process Technology
High cost of renewable energy ◆◆◆◆ High capital intensity ◆◆◆ High cost of reducing harmful effluents ◆ High volume production with unproven technology is risky ◆ Cannot economically recover products from dilute aqueous streams High cost of downstream process changes High cost of water recycling/purification	Near term profit mentality ◆◆◆◆ – politically motivated research agendas Lack of government funding for basic research ◆◆ Poor communication between industry and academia ◆ Poor understanding between chemists and bio-chemists ◆ Regulations are short-framed/short-sighted No government policy in place to drive change Land conflict - food versus chemical supply No models for collaborations between industry/academia/ government Poor information exchange between industries Policies and regulations sometimes conflict between agencies (and within agencies) No major attempt to locate power facilities near chemical users	No biomass refining industry ◆◆◆◆◆ Annual crop supply is seasonal Bio-feedstocks are not uniform Infrastructure is not in place for delivery of bio-feedstocks Drying biological feedstocks is inefficient/expensive Crops grown in different parts of the world are different Internal combustion engines used to harvest bio-feedstocks are inefficient	No good targets for transformations ◆◆◆ Bio-polymers may not be equivalent (quality, cost) to petro-polymers Health/environmental impacts of bio-polymers are not known Lack of good uses for lignin Lack of integration of the co-products from biomass	Few catalysts for CO_2 and C1 conversion ◆◆◆◆◆◆ – Methane selectivity is a problem Lack of processes for achieving high selectivity ◆◆◆◆ Barriers to efficient separations (both biomass and C1 systems) ◆◆◆◆ Catalysts are easily poisoned ◆◆◆◆ No good catalysts for processing sugars ◆◆◆ Basic understanding of bio-catalysis needs further development ◆◆◆ Too much O_2 in feedstocks which makes conversions to comparable product difficult ◆◆ No process for depolymerization of lignocellulosic materials ◆ CO_2 chemistry is poorly understood ◆ No good continuous biochemical processes Lack of industrial R&D on the utility interface Lack of ways to effectively use waste (sequester CO_2 or pollutants) Physical difficulty in processing renewables Process models do not have accurate data libraries – models are not adequate

Exhibit 2-13. Barriers/Alternative Raw Materials/Engineering

(**Top Priority,** *High Priority*, Mid Priority)

Raw Materials Related	Separations	Design, Modeling, Process Control	Reactivity	Products Related	Economics
Molecular structure of biomass **– recalcitrance** **– presence of oxygen** **– oxygenated** **– feedstocks preclude fuel development** **– low energy value due to moisture** **Stability of the methane molecule** *Inhomogeneity of feedstocks require separations and clean-ups* *Difficult transportatability and collectability of certain raw materials* *CO_2 concentration methods are too expensive (especially at low purities)* *Diffusiveness of resources, energy, and materials* *Inadequate solids and materials handling equipment* *Knowledge of toxicity of biomass materials is poor* *Unforseen effects of new processes, particles, and genetically modified organisms* *Dependence of supply on climate, seasons, and weather changes* *Mindset of technologies to break molecules down like petrochemical industry* Soot formation Future competition for aerable land area	**Efficiencies of current product recovery techniques are too low** **– especially for very dilute solutions** **– fragility, friability** *Economic separation of isomers where one is toxic, the other effective* *Feedstocks are hydrophillic, demanding a new emphasis on aqueous systems* **POLICY BARRIERS** **Uncertain tax structure for R&D** **– no stability** **– incentive is too low** Domestic use preferences on technology supported by government matching funds The broadness of U.S. patent system prevents competition	**Difficulty in predictive modeling and simulating bio-based processing** *Feedstock intermediate and product property databases for use in design* *High percentage of breakthrough technologies are needed* *Lack of process controls for bioprocessing* *– inadequate analytical techniques* *– lack of on-line monitoring* *– lack of respirometry* *Need for new manufacturing technology* *– scale-up issues* *Design concepts for integrating unit operations* *– inapplicability of traditional unit operations to biological separations* *– traditional chemical engineering approach to unit operations in universities* *Lack of demonstration of scalable systems* Consistent systems engineering approach is lacking Dissemination of information about technology and specific properties is difficult	**Low thermal efficiency of C1 processes** **Today's catalysts are inadequate and not bio-derived** *Inefficient bioreactor design* *Biomass gasifier technology is inadequate* Low product yields **SOCIETAL BARRIERS** *Unwillingness to try new technologies* Public fear of anything biotech False alarmists and fear of the unknown Local political reluctance to grounds-up plants Aesthetics of new plants	*Dominoing quality issues* *– nobody wants to be first* *Reluctance to displace existing end product uses* *Providing pilot-scale samples for application testing* *Inadequate structural properties* *– mechanical fragility of most cellulose products* Trace oxygenates in many commodity chemical processes Product stewardship - fear of liability for a completely new approach Companies lack creative approaches to considering the function of their products Longevity of structural an d coating materials Inadequate hydrogen storage methods – weight is too high – pressure is too high	**Industry is too focused on short-term profits** **– pressure for short return on R&D** **Reluctance to replace existing manufacturing infrastructure** *Energy cost for C1 processes is too high* *Large plant construction time and logistics* *Cost structure of existing chemical industry* *Difficulty in forming multi-company alliances to solve problems* Concerns for need for simultaneous development of related technologies Economic models that incorporate soft issues are lacking Adaptation of superior supply chain management to this industry does not occur

3 Research Needs for Alterative Technology

Exhibit 3-1. R&D Needs: Alternative Cleaning and Dissolution Methods (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)				
Time Frame	**Chemical science Science**	**Process/Equipment Engineering**	**Modeling/ Stimulation**	**Research Support**
NEAR (0-3 Years)	Identify and develop additional modifiers for dense phase fluids to enhance functionality ✪●●○○○ – to enable operation at lower pressures, temperatures – to enhance application-specific cleaning – to enhance substrate appearance and functionality Conduct empirical observations of garment cleaning – near term effort to conduct preliminary assessment of the cleaning process Study effects of process parameters – morphology of textiles ●○	Development and testing of dense phase fluid components capable of handling material and debris ✪✪✪● – pumps – compressors – valves – heat exchangers Conduct materials testing program for compatibility ✪●○	Develop process economic models to compare existing or emerging technology ●●○○○ – energy – cycle time – equipment – throughput – life cycle technology	Encourage professional societies and other organizations to promote manufacturing of components ○ Examine and research end user needs

Exhibit 3-1. R&D Needs: Alternative Cleaning and Dissolution Methods (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)				
Time Frame	**Chemical science Science**	**Process/Equipment Engineering**	**Modeling/ Stimulation**	**Research Support**
MID (3 -10 Years)		Improve optimization of process parameters ●○○○○○ – flow, temperature, pressure – solvent composition – level of cleanliness Optimize ancillary unit operations ●○○○ – filtration – distillation – heat transfer – adsorption QA/QC product verification ○○ – optimize and develop on-line process sensors Develop better ways to measure properties of substrates under process conditions	Develop better equations of state models for complex, DPF systems ●○ – to handle heterogenous mixtures – not simple extensions of petroleum models	Institute national training program for servicing curricula ✪○ – vocational technical training curricula Develop application - specific protocols for cleanliness targets
LONG (>10 Years)				Conduct research on alternative product design for cleaning (design for cleaning)
ONGOING	Study the kinetics and thermodynamics of mass transport processes ✪✪●●○ – time limits – mass transport – polar/non-polar soils – surfactant behavior – diffusion coefficients – viscosity – leading to dissolution rates Develop a solubility database ✪●●●	Develop alternative (commercial) materials for pressure vessels – composites – ceramics – improved steel alloys	Develop DPF process simulation capability ● – more generic widely available models	Conduct health, safety and risk research for DPF ●○

Exhibit 3-2. R&D Needs: Alternative Reaction Media in Chemical Synthesis

(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Chemical Science	Exploratory R&D	Process/Equip-ment Engineering	Modeling/ Simulation	Research Support
NEAR (0-3 Years)	Develop combinatorial lib/screens for ionic liquids ○	Demonstrate differentiated examples of key chemistry - e.g. reduction-oxidation ✪✪✪✪○ – base or acid catalyzed – selectivity change – improved yield enabling technology Explore modification of materials with alternating media-morphology changes ✪✪ Conduct systematic screening of chemistries and fluid systems ✪●○ Investigate activation of CO_2 for generation of polyesters and poly-carbonates ●● Investigate thermally stable phase transfer catalysts ● Explore commodity chemicals property modification in dense phase fluids ● Investigate recovery and products from ionic liquids ○○○ Explore the possibility of raising the viscosity of CO_2 by 1-3 orders of magnitude ○ Explore the use of light or chemical triggers to recover dissolved products from dense phase fluids/ILs			Identify industrial needs ✪●●●●○○○ Establish a clean synthesis center of excellence ✪●●●○○○ Foster cooperative academic/governm ent/industry research efforts ●●●●●●○○ Develop tools for life cycle analysis ●● Create (continue with) dense phase fluids expert subgroup as part of "Green Chemistry Institute" ● Interest researchers in working on ionic liquids ○○○
MID (3-10 Years)	Collect and publish needed thermo-kinetic data – literature – experimental – data base ●○○○	Explore economics and liability of reactions in H_20 at a large scale (non-emulsions)	Develop scale-up for specific applications (reactions) ✪✪○ – 1-10 Kg Develop new equipment designs (lower cost) ✪●○	Develop engineering cost models for supercritical fluid equipment ● Evaluate various modeling programs for potential	Identify advantages of ARM, provide comparison with known systems, and quantify evaluations ✪●○○ Define metric that will give a value to the "green"

Exhibit 3-2. R&D Needs: Alternative Reaction Media in Chemical Synthesis (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	**Chemical Science**	**Exploratory R&D**	**Process/Equipment Engineering**	**Modeling/ Simulation**	**Research Support**
	Develop experimental designs to provide data needed for modeling ✪ Define categories of reactions in new media (rates, selectivities) ●○ Develop thermodynamic property data on alternative media		Develop innovative reactor designs or materials to reduce capital cost ●○○ Conduct research on how to scale up reactions (e.g. solids handling, continuous processes) ● Design solids handling in supercritical fluids process ○○ Benchmark ARM to increase knowledge of solvents and systems ○ – cost and environmental comparisons ARM /traditional Develop pH control for CO_2 - H_2O systems Demonstrate an application in coatings	application to dense phase fluid/ARM systems ●○ Study application of corrosion models in A.R.M. ○ Develop thermodynamic model for ionic liquids to narrow potential structures for a given application ○ Develop software tools to differentiate "green" and economic advantages Develop simple lab tools for trying dense phase fluid/ARM systems Model phase behavior of dense phase fluids in complex compositions	attributes of dense phase fluid technologies ●
LONG (>10Years)	Conduct studies of interfacial science – Surface Design – Nucleation – Stability of colloids – Interfacial tension – Emulsions – Fibers – Composites – Thin films (coatings) ✪●○ Study behavior of biomass (liquid, carbohydrates, etc) in ionic solvents at different temperatures and	Explore chemistry at interfaces and in multi-phase system ✪●●●●● Study material property as a function of method of synthesis, including properties of foams ●○ Study impact of fluid properties on catalysis ○○○ Explore chemical interaction of supercritical CO_2 and/or CO_2/co-solvent system with different feed materials ○		Develop predictive techniques and supporting data for separations ✪✪✪○ Develop integrated plasma-surface-catalysis models ●	

Exhibit 3-2. R&D Needs: Alternative Reaction Media in Chemical Synthesis (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	**Chemical Science**	**Exploratory R&D**	**Process/Equip-ment Engineering**	**Modeling/ Simulation**	**Research Support**
	pressures in the presence of reagents ✪● Investigate what makes a compound very CO_2 soluble at the molecular level ○○○ Increase knowledge of transport properties ● Study phase transport phenomena (facilitation)	Develop catalysts for phase separation (include solubility of catalyst) ○ Explore materials compatibility issues ○ Explore heterogeneous polymerization – control morphology – stabilizers – composites			
ONGOING	Gather physical/chemical data for additional reaction systems ●●●○○ – stability data for "ARM" Explore new chemistries ✪●●●● Develop health/safety toxicological data on ARM ○○ Search for undiscovered environmentally benign alternative media ○○	Conduct exploratory research on alternatives to dense phase fluids (e.g. water, ionic media, fluorocarbons with different solubilities) Explore recovery, recyclization and reuse	Develop sensors and process controls ○		Disseminate information on successful laboratory applications (applied R&D) ✪○ Translate laboratory curiosities and connect with industrial needs ○○ Compile data on successful applications of dense phase fluids/ARM ○○ Develop assessment schemes through inter-society initiatives Study environmental consequences of ARM

Exhibit 3-3. R&D Needs: Alternative Material Modification/ Pollutant Sequestration (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)			
Time Frame	**Chemical Science**	**Process/Equipment Engineering**	**Modeling/Simulation**
NEAR (0-3 Years)	Optimize processes ●	Explore materials compatibility ✪○○○ – equipment materials – materials being processed – evaluate materials with respect to the process and vice versa Address large area reactions ●○○ – evaluate existing available methods – develop new methods Develop closures ○ – identify better materials of construction – develop rapid (10-60) closures	Develop a process optimization model ●●●○
MID (3-10 Years)		Develop separator technology ○○○○○○ – increase selectivity, recovery, energy efficiency, speed Design/optimize pumping and compressing equipment ●○○ – inexpensive pumps, faster compression/decompression	
ONGOING		Develop continuous processing ✪✪✪●●○○○ – bulk solids – large dimension products	Conduct studies in computational modeling ✪●●●○ – statistical mechanics ○ – more sophisticated physics based models – uncontained dense phase conditions ● – theoretical methods for complex fluids ✪ – quantum mechanics – equations of state Conduct experimental verification of models ●●●○○ – theoretical and experimental work should be carried out in concept – uncontained dense phased conditions – experimental/theoretical teams ●○○

Exhibit 3-4. R&D Needs to Overcome Key Barriers: Electrotechnology & Alternative Conditions					
Time Frame	**Lack of Efficient Separations for Dilute Solutions**	**Lack of Socially Acceptable Nuclear Energy**	**Lack of Energy Storage Technology**	**Lack of Efficient Catalysts for Moving an Electrochemical to a Photochemical Process**	**Lack of Understanding of Electrochemical Surface Phenomenon for Scale-up**
NEAR (0-3 Years)		Educate environmentalist so they can lead Develop appropriate "green screen" Perform behavior research Design breeder reactor that is standardized and demonstrated - Rethink thorium cycle Develop uniform nuclear power design for national standardization Develop better radiation construction material Develop good scalable corrosion models (thousands of years) Develop plan for decommission ing plants		Explore high quantum efficiency for light capture and efficient charge separation processes Locate controllable low-pressure, partial oxidation catalyst with selectivity Locate additional photo catalysts	Investigate effects of impurities on electrochemical material properties Investigate properties that limit efficiency increases in scale-up
MID (3-10 Years)	Identify growth factors for optimization Develop more efficient distillation Develop better model biosystems for process design, prediction, and control Develop selective membranes for complex materials Understand affinity	Explore beneficial uses of tritium Develop better containment for intrinsic safety disposal Demonstrate "modular" gas cooled reactor that is inherently safe and cannot go critical (no water container)	Develop synergistic process to use cold from LNG Develop light weight hydrogen storage Develop high pressure hydrogen storage in fail safe mode Develop an inexpensive hydrogen detector Explore the use of gas hydrates for	Mimic enzymes to design reliable and efficient catalysts Develop basic data on the role of acceptors (efficiency and selectivity) Locate a catalyst that uses electricity for redox reactions (FE_3-FE_5) Determine if microwave effects on catalysts are due to thermal effects or something else Study degradation, poisoning, and	Improve membrane and electrode life Explore miniaturization of cell gap width Investigate energy management system design (e.g., smart battery) Develop innovative designs for structural integration (battery part of structure) Design alternative electrode configurations and geometry Investigate integrated

Exhibit 3-4. R&D Needs to Overcome Key Barriers: Electrotechnology & Alternative Conditions					
Time Frame	**Lack of Efficient Separations for Dilute Solutions**	**Lack of Socially Acceptable Nuclear Energy**	**Lack of Energy Storage Technology**	**Lack of Efficient Catalysts for Moving an Electrochemical to a Photochemical Process**	**Lack of Understanding of Electrochemical Surface Phenomenon for Scale-up**
	separations Determine how to combine technology with biotechnology effectively (e.g., use microbes to decompose difficult chemicals)		transport storage Develop an efficient, cost-effective auto battery Investigate hydrogen fuel cell combinations Develop safe fly wheels	regeneration mechanisms for catalysts Investigate metal doping to create a hot spot -- develop ability to cause reactions at defined reaction sites on the surface Demonstrate nanoscale construction and design for large surface area heterogenous catalyst	design and manufacture of electrochemical cell
LONG (>10 Years)	Develop efficient active transport mechanisms across membranes that are as efficient as biological systems Avoid phase change in separation	Develop a nano-size nuclear power source for point-of-use and multi-use applications Investigate spent fuel handling so it takes up less space and is safer Resurrect spent fuel reprocessing Encourage by-product reuse	Develop an efficient natural-gas-to-solid process to avoid pressure for easier transport Explore the use of magnetic fields or capacitors (i.e., electric field) for synergistic use as a power source Develop energy storage capability similar to the compact 3-d folding of protein for use as a high energy compound Develop economically attractive process for remote natural-gas-to-hydrocarbon liquids Investigate direct one-step oxidation of methane to methanol (not syngas)	Develop efficient ways to use photosynthesis in near opaque conditions Use surface science to define and understand catalysts Investigate photosynthetic semiconductor coupling for energy-direct plugs Utilize existing biosystems and connect to manmade systems (bio/synthetic symbiosis) Rapid screening techniques for evaluating “green” reactions (combinatorial chemistry)	Demonstrate scale-up of solid state batteries Develop better high temperature batteries (new materials)

Exhibit 3-4. R&D Needs to Overcome Key Barriers: Electrotechnology & Alternative Conditions					
Time Frame	**Lack of Efficient Separations for Dilute Solutions**	**Lack of Socially Acceptable Nuclear Energy**	**Lack of Energy Storage Technology**	**Lack of Efficient Catalysts for Moving an Electrochemical to a Photochemical Process**	**Lack of Understanding of Electrochemical Surface Phenomenon for Scale-up**
ONGOING	Determine how to clean up waste streams in non-traditional ways or avoid them Conduct research on separation of organic compounds (acids) from dilute solutions	Promote sustainable power plants Continue fusion research Maintain science and engineering expertise Educate the public		Improve computation tools for rational catalyst design Replace platinum -- find more base metal catalysts	Improve regeneration of batteries

Exhibit 3-5: R&D Needs to Overcome Key Barriers: Electrotechnology & Alternative Conditions			
Time Frame	**Controlling Interfacial Reactions at the Surface (Phase Transfer Catalysis)**	**Chemical Science/ Modeling/Simulation**	**Process Design**
NEAR (0-3 Years)			Determine energy requirements for microwave assisted reactions
MID (3-10 Years)	Investigate further: ozonation reactions at the liquid layer (e.g. reaction constants) Look at reactions that can be done with ozone – splitting double bonds – safer, greener reactions Explore ways to control ozone reactions Explore new reaction media for electro-synthesis		Investigate continuous processing methods using electrotechnology Conduct 2nd phase R&D, including customers, equipment manufacturing, and scientists
LONG (>10 Years)	Fully investigate non-conventional reaction conditions – new approaches to rapid screening – ability to model on-line – control mechanisms – micro-gravity reactions		Find ways to resolve the problem of liquid diffusion coefficients (10^{-5}) – resolve transport issues – overcome diffusion control problems
ONGOING	Understand interaction between electro/magnetic fields and interfaces – particularly between fluids and solids Better understand advanced electro-based techniques: – are they more selective? – are they more efficient? – example: what are the effects of lasers on reactions? Develop electrolyte systems with out purification problems	Concerted effort at molecular modeling to design processes, especially “green” processes - Design molecules - Reduce the number of experiments to evaluate “green” technology - Develop accurate, predictive capability for large molecules that links results to “green” processes and links results to economic parameters (i.e., economic model) - Environmental “flags” for toxicity to calculate byproducts and yield	Examine/develop dielectric constants of mixtures, – examine physical properties

Exhibit 3-6. R&D Needs to Overcome Key Barriers: Electrotechnology & Alternative Conditions					
Time Frame	**Meager Under-standing of Electro-Reactor Design**	**Poor Understanding of Electro-catalysts**	**Materials Limitations**	**Insufficient Systems Design**	**Scale-up Issues**
NEAR (0-3 Years)		Establish multi-disciplinary groups to couple electrochemistry to other analytical techniques Create an organization for the exchange of ideas on electrocatalysis	Conduct efforts in materials development and characterization Develop an inexpensive porous electrode	Design systems for remote sensing – measuring voltage, temperature, electric potential	
MID (3-10 Years)	Explore ways to obtain a good surface to volume ratio	Explore better techniques for catalyst characterization under realistic conditions Apply combinatorial techniques to electro-catalysis Develop new analytical tools that take advantage of micro devices (lab on a chip)	Create self-repairing membranes Develop more stable anodes Explore and develop materials that can be tailored through molecular imprinting	Devise in-situ measurement techniques Design and develop holistic sensing methods – micro-reactors in parallel for sensing	Develop adequate process models – requires adequate process/property data Create novel designs for reactor that are scalable Seek to take more advantage of economies of scale
LONG (>10 Years)		Establish strategies for providing appropriate technical assistance on new plant construction Seek alternatives to precious metals in catalysis and other applications	Develop materials with unique properties (i.e. conductivity, resistivity) – higher conductivity electrodes	Develop techniques for coupling of unit operations	
ONGOING	Optimize reactors with respect to forces driving the reaction Devise means for more uniform delivery of energy Facilitate reproducibility of reactions Maximize productivity	Explore new catalyst designs	Reduce cost of materials while maintaining performance Increase membrane life, lower membrane mechanical damage		Seek reduction to practice (prototype)

Exhibit 3-7. Research Needs: Polymer Modeling (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	Data	(What Is Green?) Problem Definition Needs For Data	Model Development Needs	Characterization/ Measurement Tools	Institutional Education
NEAR (0-3 Years)		Compile description of current modeling capabilities ○ Define priority green chemistry problems ✪✪ Data on highest use polymers Data on highest emissions and release products Data on highest waste general products Focus on growth industries Define requirements of models for wear ability and durability Define what is recycling/ consequences for polymer properties Define "benign" as parameters for models Define modeling needs for batch processes	Life-cycle cost/benefit models ● Finer-grained CFD approach to capture properties ● Models for alternative reaction media and condition ●● Develop solvent-free processing methods/simulate Models of different release of additives from polymer Algorithms for organizing large data sets "data mining"	Atomic basis sets for metals	Industry/end-user appreciation of utility of modeling ✪✪✪✪●
NEAR-MID			Methods for "many degree of freedom problems"	Accelerated test methods for toxicity and durability	

Exhibit 3-7. Research Needs: Polymer Modeling (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	**Data**	**(What Is Green?) Problem Definition Needs For Data**	**Model Development Needs**	**Characterization/ Measurement Tools**	**Institutional Education**
MID (3-10 Years)	Control samples for characterization data Collect data on VLE		Need a group contribution model for solvents ●●○ Develop force fields from electronic structure ○ Handling com-plexity and diversity of entire system of reactions ●○○	Way to track processing history of a material	
LONG (>10 Years)	Micro structural properties data and defect, fracture property data ○○		Formulation models for additives (interactions) ● Build wear ability and durability models – photo degradation – diffusive release	Methods to measure additional micro structural properties ● Ability to measure physical and mechanical properties in line ✪✪●●	
ONGOING	Data on reactivity and catalyst performance Data and relationships for interaction with additives ●○○ – colorants – fillers – dyes – flame retardants – molecular structure – features of each Develop benchmarking data ✪○	Prioritized targets for property data ◆ environmental insults	Predictive models for reaction pathways ✪✪ – degradation pathways – synthesis – include intermediates Develop integrated models at multiple scales ✪✪✪✪ Development of hybrid models ●●○○○ Faster processing speeds ✪○ Analytical modeling Value of information models (sensitivity/uncertain ○○		Get industry comfortable with approximations Money – commitment to theoretical modeling in industry – commitment to more basic research

Exhibit 3-7. Research Needs: Polymer Modeling (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	**Data**	**(What Is Green?) Problem Definition Needs For Data**	**Model Development Needs**	**Characterization/ Measurement Tools**	**Institutional Education**
			Validation of appropriate ranges of applicability of models (fluid behavior) Predict macro properties from molecule properties ✪●●●○○○ Need ability to predict microscopic properties from molecular structure Better understanding of rheological behavior and appropriate technology to model performance		

Exhibit 3-8. Research Needs: Improved/Benign Polymer Processing/Synthesis
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Basic Science	Process Engineering Needs	Catalysis	Applications	Institutional/ Education
NEAR (0-3 Years)	Study of natural polymer properties relative to structure ○	Develop needs in plant transformation to speed up R&D/production ○	Review catalyst use in polymers assess environmental impact solve if necessary ✪●○ Database of catalyst utilization in polymerization environmental impact	Immobilized enzymes for polymerization ✪● Polymer use in soil protection erosion limits/ water infiltration Polysaccharide new applications evaluation versus synthetic polymers ✪●	Consortium of industry/ academia/ government to fund area ✪✪✪✪✪ ●○○ Inter-disciplinarian approach (team) to solve bio-polymers need/problems. (funding) ✪✪✪✪●●○ – flexible platforms for teams – exchange of people
NEAR - MID	Research on natural polymer modification structure/property ✪●● Reliable characterization of smaller quantity of material processing applications ○○	Improve method of life-cycle analysis of new versus existing 0-5 years ✪✪✪○○● – life cycle analysis tool New processes for CO_2 in chemical/polymer synthesis ✪●○○ Genetic engineering approaches to avoid out crossing	Deceased combinatorial chemistry techniques applied to catalysts enzymes ✪✪●○ Combinatorial methods for catalyst development ✪●○	Green-very selective solvents ● Replace heavy medallions in coatings with natural based biocides (also catalysts?)	Synthetic catalytic chemistry disciplines improved cooperation ●●●○
MID (3-10 Years)	Better understanding of structural requirements for biodegradability ✪●●○○○ Controlled phase transition ●	New separation purification technology needed for bio-mass ✪✪●●●○○ Total utilization of biomass polymers chemicals energy ✪●●●○○ Alternative feed stocks for monomers ✪●●○○	Flexibility of natural catalysts to conduct unnatural reactions ✪✪○	Natural polymers for coatings/adhesives surface properties ● Expand knowledge of applications for suspension/enulvar polymerization ● Design of polymeric based insecticides/ pesticides lowered environmental impact ●○	

Exhibit 3-8. Research Needs: Improved/Benign Polymer Processing/Synthesis
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Basic Science	Process Engineering Needs	Catalysis	Applications	Institutional/ Education
MID-LONG	Understanding of polymer metrics can be better designed for cell growth/differentia✪			Development of stimuli-responsive polymers "smart materials"	
LONG (>10 Years)	Research into light driven polymerization ✪○○○○○ Improved toxicity testing/study natural polymers ✪○ Use of high thorough put screening for the nonrational design of polymers ●●○ Study Human sensitivity (allergy) to bio-derived polymers ○● Study host-quest interactions database of structure/property relationships for proteins	Genetically enhanced plants to produce final product – no conversion necessary ●●○○ Replace heavy metal ions with low Mw lower toxicity systems in polymeric systems ✪	Catalysts to polymerize lower purity monomers (eliminate separation process) ✪✪✪●●●○ Develop catalysts for C1 chemistry ✪✪✪●●○ More robust (green) biocatalytic methods for convenience of complex biomass streams Natural catalysts for non-classical applications bio-patterning		
ONGOING	Metabolic engineering to control structure and features ✪✪✪✪✪✪ ✪✪●●●● New polymer synthesis from natural (biv) product denied monomers ✪✪●●● ○○○○○○ Fundamental processes controlling self-assembly ✪●○○ Search for new bio-polymers in the environment ✪●○ Study/understand genome ●●	Design criteria for production of bio-based technology products ●○	Better mechanistic understanding of enzymatic catalysis for polymer production ✪✪✪✪✪●● ○ Control of 3-D chemistry needs improved capabilities/green processes stereo-speir ✪ Techniques for measurement of surface properties catalyst/bio-polymers etc. ○○	Look for natural polymers to solve emerging application LC, NLO, photo sensitive etc. ✪ Develop improved/new "green" concepts for additives ✪ Better understanding of market/application property profile needs ○	Integration of genetic engineering capabilities with polymer needs 0-20 years ✪●● Initiate funding educational issues in polymer ecology ● Polymer scientists should now have biological science training ● Definitive results/proof of global warning problem will drive future programs

Exhibit 3-8. Research Needs: Improved/Benign Polymer Processing/Synthesis (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)					
Time Frame	**Basic Science**	**Process Engineering Needs**	**Catalysis**	**Applications**	**Institutional/ Education**
	Computational modeling of natural polymers predict properties ● Assembly - disassembly of biological macromolecules ○ Metabolic pathway kinetic modeling		Redesign of existing enzymes for new polymer applications	Environmental toxins - study impact of polymer additives ○ Natural/synthetic polymer compatibilization also natural/natural	

Exhibit 3-9. Research Needs: Alternative Reaction Media Polymerization (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)				
Time Frame	**Needs Assessments**	**Process Design/ Development**	**Material Design**	**Basic Science/ Chemistry of Reactions**
NEAR (0-3 Years)	Develop industry list of highest polluting reactions (top ten) ○ Analysis of EPA ranking criteria for "green" ○ Need sources of emissions categorized by polymer groups	Process monitoring and process control ✪●○ Need to use extruders as reactors ●○○ Need to recover rejected parts – painted/coated parts Use polymers to sequester "undesirable" materials Need a means for rapid process scale-up – pilot-plant accessibility Better classification of waste streams Study effect of solid-state orientation Need to induce crystallization/ nucleation	Develop and improve solvent-free coatings and films ✪✪✪●● New compatibilization agents ● Need thermosets that are stable at room temperature and don't require high temperatures for curing Development of multi-component solvent-free coatings Need nano-composites for improved properties Dendritic polymers to reduce viscosity – colorants – processing aides Develop electrically conductive polymers for solvent less coating	Need to know properties of polymer mixtures at high temperatures and pressures ✪✪ Need supercritical fluid properties of non-hazardous materials ○ Define solvent properties for polymers and compare to VOC data ○ Need rheological studies for polymers at critical conditions Need classification of reaction media in terms of solubility properties Need to know what kind of chemistry can be done: i.e. at a supercritical CO_2/solid interface
MID (3-10 Years)		Need low-emission, high-mobility, continuous processing ✪✪✪●○○ – CO_2 and related as an example Processing methods, for bio-based materials ✪●●	Need reversible plasticizers – that can be thermally or photolitically decomposed	Use combinatorial methods for A.R.M. (Or catalysts) "Green" separations ✪●● Need reactions in the foam state Physical properties of biomass needed Need to identify alternatives to chlorinated solvents
LONG (>10 Years)				Need catalysts for C_1 feed stocks ●● Learn how to chemically activate CO_2

Exhibit 3-9. Research Needs: Alternative Reaction Media Polymerization
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Needs Assessments	Process Design/ Development	Material Design	Basic Science/ Chemistry of Reactions
ONGOING	Develop libraries of polymer processing needs and green (A.R.M.) Alternative Reaction Media – toxicity data – physical properties Need to measure the cost-benefit relation of "green"	Need programs for developing solvent-less processes ✪✪✪●●● ●●○ Development of processing methods to alter polymer properties ✪✪✪●○○○ Need to improve recycling processes ○ Differentiated examples of A.R.M. – also measure economics		Study of chemistry in A.R.M. ✪✪✪✪✪✪✪✪✪●● ○○○ Need a complete characterization of A.R.M. ✪●●○ Research on property relationships ✪●○ Need better measurement techniques ✪○○○○○○ Study types of processes that can be used with A.R.M.

Exhibit 3-10 Research Needs/Alternative Raw Materials/New Science
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Biomass	C1 (emphasis on CO_2) & Small Molecules	Enabling Science
NEAR (0-3 Years)	Identify properties of biomass products and compare to properties of current commercial products ● Conduct research and technology science to ensure that products can be isolated on a large scale from biomass and or H_2O	Develop catalytic processes, including catalyst and reactor design for chemical synthesis from C1 molecules ✪✪✪✪✪✪●○○○	Develop high thru-put methods for catalyst synthesis and testing ●●●●●○○○○ Develop computational capability for mechanistic reactions
MID (3-10 Years)	Molecular catalysts for biomass processing e.g. High temperature homogenous hydrolysis catalysts for selective degradation of cellulose; and develop new non-salt generating selective catalytic chemistry for conversion of biologically derived material especially oxidation reduction chemistry ✪✪✪●●●●○○ Increase the efficiency of biocatalysts useful in processing biomass and down stream products – increase the carbon efficiency of bio-processes ✪✪○○○ Design organisms that single handedly convert biomass to useful chemicals without extensive chemical processes. Develop consolidated bio-processing for onestep biological conversion of pretreated cellulosic biomass to useful products without exogenous cellulase or other catalysts ✪●○ Improve separation science for water soluble materials (e.g., from biomass fermentation) ●●●●○ Develop methods for handling charged ionic species in solution on a large scale (e.g., separations) Develop cost-effective processing technology for integrated collection and transportation of biomass Develop economical processes for conversion of lignin to aromatic carboxylic acids and other monomer feedstocks ○	Develop high activity catalyst for selective CO_2 co-polymerization ✪✪ Pursue understanding of M-C bond formation from CO_2 ✪●○○○ Develop capability to use formate esters and other CO_2 derived molecules as fundamental building block ●●●○○○○○ Develop cost-effective synthesis of dimethyl carbonate from CO_2 and demonstrate as fuel or fuel additive ●○○○	Develop cheap methods of production and selective catalystic methods for the usage of H_2O_2 ✪✪✪○○○○ Develop high-performance metal catalyst for biphasic processes ● Develop methods of O_2 control for delivery and removal to reactors Explore and understand depolymerization mechanisms ●●○○○

Exhibit 3-10 Research Needs/Alternative Raw Materials/New Science (✪ = Top Priority; ● = High Priority; ○ = Medium Priority)			
Time Frame	**Biomass**	**C1 (emphasis on CO_2) & Small Molecules**	**Enabling Science**
LONG (>10 Years)	Develop manipulation of metabolic pathways to design and add value to plants/biomass used for chemical feedstocks ✪●●●○○○ Develop cost-effective processes for the conversion of biomass to useful lower molecular weight chemical feedstocks Determine how cellulase can be modified to avoid product inhibition	Develop generational recovery of H_2 from H_2S ○ Develop catalysts for reactions of CO_2 and H_2 to form non-cyclic oligomer of CHO	Develop catalysts for efficient photo decomposition of H_2O into H_2, and photochemical CO_2 fixation ✪✪✪✪○○ Develop catalysts for the efficient conversion of solar to chemical energy (non-nuclear) ✪✪✪● Develop selective catalytic oxidation of organic matter using O_2 ●●●●○○○
ONGOING	Explore selective transformation and functionalization of carbohydrates ✪✪✪✪○○ Develop economical pathways to produce aromatic hydrocarbons from biomass Overcome recalcitrance of cellulosic biomass via new high-impact approaches relevant to: – pretreatment and enzymatic hydrolysis – gasification – catalysis – acid hydrolysis	Develop processes to synthesize polymers derived from CO_2 with properties similar to petroleum -derived analogs	Develop new computational and experimental tools to speed catalyst design and testing ●

Exhibit 3-11. Research Needs/Alternative Raw Materials/Processing Alternatives

(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	CO_2 Utilization	Policy/Funding	Polymers	Systems Analysis/ Modeling	Bio-Refining	Catalysts	Separation & Processes	Genetics
NEAR (0-3 Years)	Establish integrated program for CO_2 utilization ✪✪●●●● – between direct users, plant growers, sequestration users – framework to develop balance – better communication Create more efficient ways of CO_2 transfer (pipelines etc..)	Create a policy initiative to address technology needs ●	Use cellulosic or polysaccharide materials as a feedstock ✪●○	Look at overall cost, energy of using alternate feedstocks ✪○ Develop real-time, on-line models to react to a process	Define what a bio-processing or CO_2 capture plant will look like	Apply combinatorial chemistry for screening chemical catalysts		
NEAR-MID				Perform computer modeling of catalyst poisoning Develop cost models for a flexible feedstock plant Find uses for the inorganic component of bio-feedstocks			Explore novel membranes that are more efficient for separating products from waste ●●○○	

Exhibit 3-11. Research Needs/Alternative Raw Materials/Processing Alternatives
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	CO_2 Utilization	Policy/Funding	Polymers	Systems Analysis/ Modeling	Bio-Refining	Catalysts	Separation & Processes	Genetics
MID (3-10 Years)			Use other polysaccharides as derivatives for materials ●○	Include total cost accounting in life cycle inventory analysis ✪● – data libraries must be established	Find cheaper ways to separate cellulose from biomass ✪✪✪✪● Combine chemistry for biomass refining process and make links with existing chemical intermediates ✪✪✪●● Lower capital cost of process from starch or cellulose to derivatives ○ Lower capital cost of processes from trees to cellulose	Develop catalysts for selective transformation of sugars ✪✪●●○○ Develop sulfur tolerant catalysts ✪● Explore means for selective C-C bond cleavage ●●●●●○ – convert sugars to formalde-hyde, ethylene glycol – break down polymers Create a larger pool of enzymes that can be used for specific purposes ●●● Create more efficient ways for understanding enzyme reactions		Develop safe gene cloning systems for various processes ✪

Exhibit 3-11. Research Needs/Alternative Raw Materials/Processing Alternatives
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	CO_2 Utilization	Policy/ Funding	Polymers	Systems Analysis/ Modeling	Bio-Refining	Catalysts	Separation & Processes	Genetics
MID-LONG			Pursue new chemistry to create a wider variety of CO_2 - based polymers ●○	Develop scalable models to go from molecular level to bulk to life-cycle (holistic modeling) ✪○		Catalysts that will form C-C, C-N, C-? bond, to CO_2 ✪✪✪✪●○ Develop catalysts for C, feedstock, ✪✪✪● – photo - catalysts – thermal catalysts – electro catalysts Develop cheaper enzyme co-factors or other methods to generate enzymes ✪○○ Eliminate or reduce product inhibition of biocatalysts	Recover CO_2 from the atmosphere ●●	Rapid genetic modifiable organism (GMO) development ✪●●
LONG (>10 Years)	Devise ways to produce cheap hydrogen ●○				Integrate genetic engineering of trees and other feedstocks with process chemistry		Recover methane from gas hydrates	

Exhibit 3-11. Research Needs/Alternative Raw Materials/Processing Alternatives
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	CO_2 Utilization	Policy/Funding	Polymers	Systems Analysis/ Modeling	Bio-Refining	Catalysts	Separation & Processes	Genetics
ONGOING	Develop better solar energy conversion technology ✪○	Promote spending for research ✪●●●○ Consider health and safety issues of alternative processing ○ Establish mechanisms for greater interaction between government, industry, academia	Support applications development for lignin based products ●○○	Conduct research to determine where capital is best used for alternate processing ●●● Pursue chemical and utilities industry integration ●○○○ Develop chemical sensors for process control ● Consider the smaller niche markets for improvements through alternatives		Conduct research to understand biocatalysis ●○○ Combine bio-catalyst with chemical catalyst reactions ○○	Lower cost of enzyme purification ○ Investigate one-step processes instead of multi-step (e.g. H_2 separation)	Pursue a better understanding of metabolic pathways Conduct research to understand gene sequence, & enzyme function to produce chemicals

Exhibit 3-12. Research Needs/Alternative Raw Materials/Engineering

Top Priority, *High Priority,* Mid Priority

<table>
<tr><th>CATEGORY</th><th>BARRIER:</th><th>NEAR
(0-3 yrs.)</th><th>MID
(3-10 yrs.)</th><th>LONG
(>10 yrs.)</th></tr>
<tr><td rowspan="6">Raw Materials Related</td><td rowspan="2">Molecular structure of biomass</td><td>Develop database for molecular modeling

Acid hydrolysis</td><td>Genetic and chemical alteration of molecular structure
Physical process
- ultrasound
- microwave
- radiation
Develop new separations process from the heteroatoms and metals</td><td></td></tr>
<tr><td colspan="3">Identify routes from existing structures to products
- platform chemical</td></tr>
<tr><td>Stability of the methane molecule</td><td></td><td>Stabilize the last precursor to methane
- understand methane formation mechanism
Low temperature combination of form and water gas shift
Biological routes to combine CH_4 and CO_2
Develop novel reactor designs that permit elevated temperature reaction.</td><td>Efficient, directed activation of CH_4
Improve short contact time conversion processes
Economically apply solar/thermal energy to high-temperature reators</td></tr>
<tr><td rowspan="2">Inhomogeneity of feedstocks require separations and clean-ups</td><td>Improve front-end mechanical systems</td><td>Improve drier processing techniques</td><td></td></tr>
<tr><td colspan="3">Explore spectrum of feedstocks (some may hold competitive advantage)</td></tr>
<tr></tr>
<tr><td rowspan="2">Processing Related: Separations</td><td rowspan="2">Efficiencies of current product recovery techniques is too low</td><td>Develop new and more efficient Absorption techniques
Separation of toxic and non-toxic isomers or enantiomers

Reactive separation
- reactive distillation
- membrane reactor</td><td>Develop highly selective membranes
Develop new methods of reversibly altering products
- e.g. laser activation, bioactivation</td><td>Robust separations for very dilute solutions of fragile molecules in processing of bulk solids</td></tr>
<tr><td colspan="3">Hybrid separation techniques combining a biological step
Apply “pinch” like techniques to purity</td></tr>
</table>

Exhibit 3-13. Research Needs/Alternative Raw Materials/Engineering

Top Priority, *High Priority*, Mid Priority

CATEGORY	BARRIER:	NEAR (0-3 yrs.)	MID (3-10 yrs.)	LONG (>10 yrs.)
Processing Related: Reactivity	Low thermal efficiency of C1 processes	*Identify new alternative reaction media (e.g., supercritical CO_2)* **Develop improved or novel bio-reactors**	*Laser activation*	**Develop low-temperature C1 conversion processes** *Develop bioreactors in which the organism is the reactor and separator*
	Today's catalysts are inadequate and not bio-derived	*Catalysts search efforts based on computational or combinatorial techniques* *-biocatalyst search*	Engineered reactor systems to protect catalysts	
		New catalyst formulations designed for renewables processing systems		
Processing Related: Design, Models, Process Control	Lack of process controls	Improved data analysis (e.g., fuzzy logic) Research on-line monitoring		
	Difficulty in predictive modeling techniques		*Central database and modeling program that is generally available*	
		Develop property database for feedstocks		
	General design issues	More reliable float control measurement of two-phase		
		Develop advanced materials of construction		
Product Related	Dominoing quality issues	*Explore industry consortia for demonstrations* Develop more relevant product specifications		
		Develop better analysis techniques for quality along the entire process		

Exhibit 3-14. Research Needs/Alternative Raw Materials/Engineering

Top Priority, *High Priority,* Mid Priority

CATEGORY	BARRIER:	NEAR (0-3 yrs.)	MID (3-10 yrs.)	LONG (> 10 yrs.)
Product Related	Reluctance to displace existing end product uses		Develop carbohydrate to alkaline process	
		Explore new product uses		
	Providing pilot scale samples for application testing is difficult	*Combination analysis of application testing*	*Establish central pilot plant facilities*	
		Miniaturize application testing		
Economics	Reluctance to replace existing manufacturing infrastructure	Examine ways to redeploy existing infrastructure Study infrastructure to identify where equipment must be replaced effort Identify specific commodity, chemicals that have large growth potential	Develop modular process deployment capabilities	
	Industry is too focused on short-term	**Total cost assessment** *Stack in parallel many of the development steps* *-combine business and engineering expertise in development teams*	*Incubator test facilities to rapidly test designs, etc.*	
		Establish information clearinghouse for different technologies More application focused verses product focused		
Societal	Unwillingness to try new technologies	-Combine social science and engineering in training students Public recognition of companies involved in this type of work		
		Education and demonstration to change society views		
Policy	Uncertain/unstable tax structure for R&D	Research in econometric models to show government the impact of tax structures		

Appendix A

Workshop Participants

John Ackerman, Argonne National Laboratory

Hussain Al-Ekabi, Science & Technology Integration, Inc.

Joseph Allison, AutoClave Engineers

Sten-Håkon Almström, Electrolux-Wascator AB

K.R. Amarnath, EPRI

Paul Anastas, Environmental Protection Agency

Mark Anderson, BOC Gases

Merrick Andlinger, Pure Energy Corporation

Klas Bäck, AGA USA

Frank Baglin, University of Nevada

Jeffrey Baird, ARCO Chemical

Tom Baker, Los Alamos National Laboratory

Karin Bartels, Degussa Corporation

Lauren Bartlett, Environmental Protection Agency

Edwin Bassler, Raytheon Corporation

Eric Beckman, University of Pittsburgh

Jacqueline Bélanger, Environment Canada

Jack Belluscio, Global Technologies, LLC

Ray Bilski, Chemical Information Services

Jeremy Boak, Los Alamos National Laboratory

Joseph Bozell, National Renewable Energy Laboratory

Marion Bradford, A.E. Staley Manufacturing Company

Joseph Breen, Green Chemistry Institute

Joan Brenneke, Notre Dame University

Vincent Brice, Akzo Nobel, Inc.

Raymond Brusasco, Lawrence Livermore National Laboratory

Steven Buelow, Los Alamos National Laboratory

Charles Byers, Isopro International

James Capistran, University of Massachusetts

Ruben Carbonell, North Carolina State University

Joseph Carra, US Environmental Protection Agency

Sidney Chao, Raytheon Environmental Systems, Inc.

Liaohai Chen, Los Alamos National Laboratory

Lalit Chordia, Thar Designs, Inc.

Howard Clark, ASME International

Geoffrey Coates, Cornell University

Terry Collins, Carnegie Mellon University

David Costa, Los Alamos National Laboratory

Bruce Cranford, CCR

Alan Curzons, Smthkline Beecham

Donald Darensbourg, Texas A&M University

Robert Davidson, 3M CorporationDaniel DuBois, National Renewable Energy Laboratory

Jayesh Doshi, DuPont, Inc.

Kevin Edgar, Eastman Chemical Company

A. Gwen Eklund, EPRI

Douglas Elliott, Pacific Northwest National Laboratory

Lawrence Farrar, Montec Associates, Inc.

Guiseppe Fazio, Nuova COMECO2 S.p.A.

Guiseppe Fedegari, Fedegari Autoclavi, S.p.A.

Stephen Fitzpatrick, Biofine/Biometics Inc.

Peter Foller, PPG

Thomas Foust, Idaho National Engineering and Environmental Laboratory

Etsuko Fujita, Brookhaven National Laboratory

Mehmet Gencer, B.F. Goodrich

Dorothy Gibson, University of Louisville

Michael Gonzalez, US Environmental Protection Agency

Douglas Haseltine, Eastman Chemical Company

Richard Helling, Dow Chemical Company

David Henton, Cargill-Dow Polymers

Darryl Hertz, Kellogg Brown & Root, Inc.

Bette Hileman, Chemical & Engineering News

Norman Hinman, BC International Corporation

Dennis Hjeresen, Green Chemistry Institute/ Los Alamos National Laboratory

Nancy Ho, Purdue University

Shuen-Cheng Hwang, BOC Gases

Larry Ito, Dow Chemical Company

Gunilla Jacobson, Los Alamos National Laboratory

Judy Jarnefeld, NYSERDA

Philip Jessop, University of California-Davis

Karl Johnson, University of Pittsburgh

Keith Johnston, University of Texas

Roger Jones, Supramics Company

John Kerr, Lawrence Berkeley National Laboratory

Laura Kramer, Los Alamos National Laboratory

Richard Kraus, Dow Chemical Company

Anil Kumar, Prairie View A&M University

Julian Lakritz, Global Technologies, LLC

Myung Lee, Savannah River Technology Center

Donald Lester, MiCell Technologies

Philip Lester, Genetech, Inc.

Chao-Jun Li, Tulane University

Viorica Lopez-Avila, Midwest Research Institute

Garry Lowe, Wittemann Company, Inc.

F.A. Luzzio, University of Kentucky at Louisville

Lee Lynd, Dartmouth College

Zenon Lysenko, Dow Chemical Company

Kimberly Magrini, National Renewable Energy Laboratory

Amy Manheim, US Department of Energy

Alexander Matthews, Kansas State University

Michael Matthews, University of South Carolina

Paul Maupin, US Department of Energy

T. Mark McCleskey, Los Alamos National Laboratory

William McGhee, Monsanto

Paulette Middleton, RAND Environmental Science and Policy Center

Melissa Miller, Los Alamos National Laboratory

Luc Moens, National Renewable Energy Laboratory

Steven Nagamatsu, Itochu Aviation, Inc.

Trueman Parish, Eastman Chemical Company

David Park, AGA Gas Inc.

Bernard Penetrante, Lawrence Livermore National Laboratory

David Pesiri, Los Alamos National Laboratory

Gene Petersen, National Renewable Energy Laboratory

Gordon Plishker, Sam Houston State University

Alexander Pokora, Organic Technologies

Steven Rice, Sandia National Laboratory

Dennis Riley, Monsanto

Lloyd Robeson, Air Products and Chemicals, Inc.

Raymond Robey, Praxair, Inc.

Robin Rogers, University of Alabama

David Ross, SRI International

James Rubin, Los Alamos National Laboratory

Charles Russomanno, U.S. Department of Energy

Endalkachew Sahle-DeMessie, US Environmental Protection Agency

Erik Sall, Monsanto Company

Anthony Sammelis, Eltron Research, Inc.

Arnold Schaffer, Phillips Petroleum Company

Thomas Sciance, Sciance Consulting Services, Inc.

Kenneth Seddon, Queens University of Belfast